



## VERIFICATION OF TRANSLATION

**German Patent Application Number 199 31 204.4**

I, Helga Malm of SASOL Germany GmbH, Roemerstrasse 733, 47443 Moers, Germany do hereby declare that I am well acquainted with both the German and English languages and I am a competent translator thereof, and that the attached document is a true and complete translation of the specification and claims of the aforesaid patent application, made by me to the best of my knowledge and belief.

Signed this 28<sup>th</sup> day of July 2004

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**PROCESS FOR THE PREPARATION OF METAL OXIDES THAT ARE  
DISPERSIBLE IN ORGANIC SOLVENTS**

5 This invention relates to a process for preparing metal oxides or metal aquoxides that are dispersible in organic solvents. The invention further relates to metal oxides or metal aquoxides that are modified with organic sulfonic acids and can be prepared by this process.

10 From WO 95/12547 or German patent DE 43 37 643-C1, a process is known for the preparation of nanocrystalline alumina hydrates in boehmitic or pseudoboehmitic form that are dispersible in water. Water-dispersible alumina hy-  
15 drates can be obtained in this process by hydrolysis of aluminum alkoxides at temperatures from 30°C to 110°C, addition of an acid (monovalent inorganic or organic acids as well as their anhydrides), and subsequent hydrothermal aging. The resultant dispersions are suitable for  
20 example for coating materials, such as glass, metal, or plastics, as well as for producing high-strength catalyst supports, pure-phase mixed oxides, or after conversion to the  $\alpha$ -form, for producing high-performance abrasives. The water-dispersibility of those alumina hydrates, which are  
25 not dispersible in organic solvents, is a disadvantage for certain applications, such as weather-resistant exterior coatings. For certain applications, aluminas that are dispersible in organic solvents but not in water are of interest.

30 The aluminas prepared by some of the processes known in the art are dispersible in dilute acids and water, and some of these aluminas are dispersible in short-chain alcohols, such as methanol and ethanol. They are not  
35 dispersible in organic aprotic solvents.

Colloidal alumina solutions in organic solvents are described for example in DE 41 16 522-C2 as well as by R. Naß and H. Schmidt ("Formation and Properties of Chelated Aluminum Alkoxides" in H. Hausner, G. Messing, S. Hirano (Eds.) "Ceramic Powder Processing", Deutsche Keramische Gesellschaft, Cologne, 1969). According to said publication, the alumina hydrates obtained by hydrolysis of aluminum alkoxides in an organic solvent and in the presence of a  $\beta$ -diketone compound can occur as colloids in the solvent. However, the colloidal solutions described there are only (meta)stable in the organic solvent at high dilutions. Only for isopropanol as a solvent has it been experimentally proven that the solutions are in fact colloidal ones. Experiments have shown that after removal of the solvent, the colloidal particles prepared by said process cannot be redispersed.

From AU 200149 a process is known for the preparation of various inorganic oxides and hydroxides that can be dispersed in mineral oils. For this purpose, inorganic oxides or hydroxides are subjected to grinding in a ball mill in the presence of a surfactant and a mineral oil as the carrier fluid. As surfactants, organic sulfonic acids are cited among others. The surfactants are added to the composition in quantities of 0.5 to 3 wt%.

In US 3,018,172, a process is described for the preparation of aluminum hydroxides that are dispersible in non-polar, high-molecular organic solvents, such as mineral oils. In said process, aluminum alkoxides in a volatile organic solvent are hydrolyzed by contact with an organic sulfonic acid, such as postdodecylbenzenesulfonic acid in

a viscous organic carrier fluid. After hydrolysis, the volatile organic solvent is removed and an aluminum  
5 hydroxide dispersed in a viscous organic carrier fluid, such as xylene, remains.

A similar process is described in US 3,867,296, wherein a high-molecular organic sulfonic acid in a viscous organic  
10 carrier fluid is added to alumina hydrates in a volatile organic medium.

US 4,076,638 and US 4,123,231 describe variants of this process. According to US 4,076,638, a carboxylic acid is  
15 used in parallel, while the viscous organic carrier fluid is dispensed with. According to US 4,123,231, an aqueous mineral acid is used in addition to the organic sulfonic acid.

20 The processes described in the aforementioned U.S. patents have in common that substantial amounts of organic sulfonic acids must be used compared to the amount of alumina hydrate. In addition, organic solvents are required for the preparation of dispersible alumina.

25 According to AU 200149, mineral oxides are taken up in highly viscous mineral oils having a high solids content and then are dispersed in mineral spirits at high dilutions with a low solids content. However, these are no  
30 real colloidal solutions.

After drying, the products obtained by the aforesaid processes are no longer dispersible in organic solvents. It is the object of the present invention to provide dis-  
35 persible metal oxides/metal aquoxides. It is a further

object of this invention to provide a process for preparing such products, which does not have the disadvantages of the prior art and, for example, does not require organic solvents for their preparation. These problems are solved by the subject matter of the invention.

Metal oxides or metal aquoxides, especially alumina hydrates, which are dispersible in aprotic or protic organic solvents are the subject matter of the present invention. Said products can be obtained by reaction of

(A) one or more metal oxide(s)/metal aquoxide(s) having a crystallite size of 3 to 100 nm, preferably 4 to 20 nm (determined by x-ray diffraction on the 021 reflex) and a particle size of less than 5,000 nm, preferably 20 to 1,000 nm, determined for example in the dispersion during the production process prior to drying

with

(B) one or more organic sulfonic acid(s), where

(i) in case the reaction takes place in a largely aqueous medium, the organic sulfonic acid is a mono-, di-, or trialkyl benzene sulfonic acid, wherein the alkyl residue(s) is (are) C<sub>1</sub> to C<sub>6</sub> alkyl residues, and the organic sulfonic acid is soluble in the aqueous medium and mono-C<sub>1</sub>-alkyl benzene sulfonic acids or mono-C<sub>3</sub>-alkyl benzene sulfonic acids are preferred, or

(ii) in case the reaction takes place in an organic aprotic solvent, the organic sulfonic acid has at least 14 carbon atoms and at least one aromatic ring,

wherein the components (A), calculated as metal oxide,  
and (B) are used at weight ratios from 99 : 1 to 60 : 30,  
5 preferably 98 : 2 to 80 : 20.

Preferred embodiments of the subject invention are the  
subject matter of the subordinate claims.

10 The solvents used as dispersants according to the inven-  
tion are:

- (I) nonprotic polar organic solvents
- (II) protic polar organic solvents
- (III) nonpolar organic solvents.

15 Suitable nonprotic polar organic solvents (I) include  
ketones, ethers, and esters, such as acetone, tetrahydro-  
furan (THF), methyl ethyl ketone, polyol ester, 1,6-  
hexanedioldiacrylate, and dimethylsulfoxide (DMSO).

20 Suitable protic polar organic solvents (II), optionally  
high-molecular ones, include alcohols, polyethers (with  
at least one free hydroxy group), hydroxyalkyl esters and  
hydroxyalkyl ketones, or carboxylic acids. Examples of  
25 suitable alcohols include ethyleneglycol, C<sub>2</sub> to C<sub>8</sub> mono-  
or dihydroxy alcohols, such as propanols, butanols,  
pentanols, and hexanols.

Suitable nonpolar organic solvents (III) are for example  
30 toluene and chlorobenzene.

The dispersible metal oxides or metal aquoxides obtain-  
able by the process of the invention are powders that can  
be dispersed in the aforementioned solvents up to a  
35 solids content of 35 wt%. The particle size of the

dispersed alumina hydrates is preferably from 20 to 1,000 nm (determined by photon correlation spectroscopy (PCS)).

5 In a preferred embodiment of the present invention, the metal oxides or metal aquoxides, especially amorphous or nanocrystalline alumina hydrates (with crystallite sizes of up to 100 nm, measured on the 021 reflex, and grain  
10 sizes between 0.2  $\mu\text{m}$  and 90  $\mu\text{m}$  with particle sizes of 20 to 1,000 nm in the dispersion) are mixed and stirred with 0.2 to 2 grams of *p*-toluenesulfonic acid monohydrate per gram of alumina or metal oxide or metal aquoxide, in each case calculated as metal oxide, at temperatures between  
15 0 and 140°C during 30 to 180 minutes, and are dried by spray drying, freeze drying, drying in supercritical solvents, filtration, or rotary drum drying. The resultant powder retains little water dispersibility (<30 wt%) and is characterized by a very narrow grain size distribu-  
20 tion. The powder can be easily dispersed in the aforementioned organic solvents with particle sizes from 10 to 1,000 nm, preferably from 10 to 500 nm (measured in the dispersion).

25 Part of the dispersions obtained in this way are translucent. They produce transparent coatings, for example on films/foils, glass, or similar surfaces. As a result of their dispersibility in organic solvents, the aluminas modified in this way are suitable for incorporation into  
30 various water-insoluble polymers or lacquers/paints.

Most of the dispersions prepared in this way are opaque. They are characterized by excellent sedimentation and centrifugation stabilities. Hence, they are genuine col-  
35 loidal solutions. Another specific feature is their

redispersibility after drying, especially after drying in organic solvents, and the possibility of making stable  
5 dispersions with a high solids content ( $> 20$  wt%). In contrast to dispersions of alumina hydrates in aqueous systems, the viscosity increases only slightly at the beginning and then remains constant after one day (see Fig. 1/1). No sedimentation occurs, even not after  
10 several weeks. Owing to these properties, the *p*-toluene-sulfonic acid-modified alumina hydrate of the invention is particularly easy to process and is most appropriate for making transparent coatings. Furthermore, it is useful as a filler in hydrophobic materials, such as PVC  
15 or lacquers/paints based on organic solvents.

#### **Dispersing Procedure**

20 Into a beaker, there were placed 18 grams of solvent and, while stirring vigorously, 2 grams of modified alumina hydrate were added in portions into the vortex within 1 to 5 minutes. The mixture was stirred for additional 10 minutes. The resultant dispersion had a solids content of  
25 10 wt%. No sedimentation will occur with readily dispersible products. Dispersibility was determined by centrifugation of the dispersion at 2,000 rpm (10 min), drying (at  $120^{\circ}\text{C}$ ), and weighing of the precipitate.

30 The term 'dispersible metal oxides/metal aquoxides' employed herein especially refers to products which, when following the procedure described hereinbefore, remain dispersed at  $\geq 95$  wt% or  $\geq 98$  wt%.



### **Example 1**

5 20 grams of water-dispersible nanocrystalline alumina hydrate (crystallite size measured on the 120 reflex: 8-12 nm) (CONDEA product Disperal™ S), corresponding to 14.4 grams of Al<sub>2</sub>O<sub>3</sub>, were dispersed in a solution of 4 grams of *p*-toluenesulfonic acid in 180 grams of demineralized water and heated to 90°C for 30 minutes with stirring, thereby adjusting the pH-value to 1.5 and moderately thickening the dispersion. After cooling, the suspension was spray dried (inlet temperature 240 to 270°C, outlet temperature <110 °C). A white odorless powder was  
10  
15 obtained the properties and dispersibility of which are shown in Table 2 and Tables 1 and 4, respectively.

### **Example 2 (PTSA-Modified Silica Alumina)**

20 Batch: 180 grams of demineralized water  
4 grams of *p*-toluenesulfonic acid (PTSA)  
20 grams of Siral™ 30 D

A dispersion of 20 grams of Siral™ 30 D was prepared in  
25 a solution of 4 grams of *p*-toluenesulfonic acid in 180 grams of demineralized water. The resultant yellowish sol-like dispersion was spray dried. The C-value after drying was 8.61%. The powder was redispersible at 99% in water and ethanol. After exchanging the solvent, it was  
30 redispersible in hexanol and ethylene glycol, too.

### **Example 3**

4 grams of postdodecylbenzenesulfonic acid (Marlon™  
35 AS-3) were dissolved in 180 grams of toluene. 20 grams of Disperal™ S were added. The mixture was stirred at 80°C

for 30 minutes. The resultant yellowish sol with a solids content of approx. 10% contained aluminum oxide particles  
5 having a size of about 195 nm (measured by PCS). The sol was at 97.3% stable to centrifugation (10 minutes at 2,000 rpm). After removal of the solvent at 40°C/77 mbar, a yellowish crystalline powder was obtained which was re-dispersible in toluene, tetrahydrofuran (THF), butanol,  
10 methyl-*tert*-butyl ether (MTBE), and trichloromethane. In chlorobenzene, a translucent dispersion can be obtained, which is not stable to centrifugation, however. The powder is 100% hydrophobic, i.e., dispersibility in water was reduced to 0% by reaction with Marlon™ AS-3. The  
15 organosols are characterized by long-term stability to agglomeration. No increase in viscosity was observed after several days. The dispersibility of the powder is shown in Table 3.

**Table 1 Dispersibility in Various Organic Solvents**

Solvent	Dispersibility (up to 10 wt% solids)	Particle Size [nm]	Transmission (0.1% solids) [%]	Remarks	Centrifugation Stability (2,000 rpm/10 min) [%]
Acetone	Yes (opaque)	80	60.6%	With 20% solids: thixotropic	94.2%
Ethanol	Yes	100	84.5%	-	99.0%
i-Propanol	Yes (limited)	-			Not determined
n-Butanol	Yes (opaque)	97			99.5%
Hexanol	Yes	335	65.8%	Thixotropic	84.6%
Ethyleneglycol	Yes (opaque)				
THF	Yes (opaque)	121			96.5%
DMSO	Yes (opaque)	104			95.0%
Chlorobenzene	By solvent exchange * (20% solids)	400		Low viscosity	99.5%
Dichloromethane	No	-			-
Toluene	By solvent exchange *	PCS not possible		Gelatinized	Not determined
1,6-Hexanediol- diacrylate	By solvent exchange *	-		Polymerized in UV	Not determined

5

\* At first dispersion in acetone, then addition of equal amounts of solvent (here: chlorobenzene), followed by displacement of the acetone by stirring with heating to 40 °C.

10 **Table 2 Physical Characteristics of the Powder**

		9.1 wt% PTSA	16.8 wt% PTSA
Specific surface area (BET) (activated for 3 h at 250 °C)	[ m <sup>2</sup> /g ]	-	135
Pore volume (0 - 1,000 nm pore diameter)	[ cm <sup>3</sup> /g ]	-	0.23
Average pore radius	[ nm ]	-	3.2
Al <sub>2</sub> O <sub>3</sub> content	[ % ]	-	66
C content	[ % ]	3.8	6.5
Particle size (dynamic laser scattering)		d <sub>10</sub> : 0.7 d <sub>50</sub> : 2.2 d <sub>90</sub> : 8.6	d <sub>10</sub> : 0.3 d <sub>50</sub> : 1.2 d <sub>90</sub> : 8.5

5

**Table 3 Dispersibility of Disperal™ S / Marlon™ AS-3 in Various Solvents**

Solvent	Dispersibility [ % ]	Particle Size (PCS) [ nm ]	Transmission [ % ]
Toluene	95.5	166	63.7
THF	99.0	113	32.3
Butanol	99.0	130	44.5
MTBE	85	-	6.8
Trichloromethane	98.5	64	42.3

10

**Table 4 Dispersibility of Disperal™ PTSA in Solvents Mixtures (10 wt% Solids)**

Solvent	Ratio	Particle Size (PCS) [ nm ]	Centrifugation Stability (2,000 rpm/10 min) [ % ]
CHCl <sub>3</sub> : MeOH	90 : 10	90	98
CHCl <sub>3</sub> : MeOH	70 : 30	70	97
CHCl <sub>3</sub> : MeOH	50 : 50	80	97.5
CHCl <sub>3</sub> : MeOH	30 : 70	107	97.5
CHCl <sub>3</sub> : MeOH	10 : 90	70	98.5
CH <sub>2</sub> Cl <sub>2</sub> : MeOH	90 : 10	97	98
CH <sub>2</sub> Cl <sub>2</sub> : MeOH	70 : 30	109	96
CH <sub>2</sub> Cl <sub>2</sub> : MeOH	50 : 50	103	96.3
CH <sub>2</sub> Cl <sub>2</sub> : MeOH	30 : 70	97	98.5
CHCl <sub>3</sub> : Acetone	70 : 30	148	84
CHCl <sub>3</sub> : Acetone	50 : 50	52	97.5

## Claims

- 5
1. A process for preparing modified metal oxides or metal aquoxides which are dispersible in organic solvents by reaction of
- (A) one or more metal oxide(s)/metal aquoxide(s) having  
10 a crystallite size of less than 150 nm determined by x-ray diffraction on the 021 reflex and a particle size from 10 to 5,000 nm, preferably 20 to 1,000 nm, with
- (B) one or more organic sulfonic acid(s), where
- 15 (i) in case the reaction takes place in a largely aqueous medium, the organic sulfonic acid is a mono-, di-, or trialkyl benzene sulfonic acid, wherein the alkyl residue(s) is (are) C<sub>1</sub> to C<sub>4</sub> alkyl residues, or
- 20 (ii) in case the reaction takes place in an organic aprotic solvent, the organic sulfonic acid has at least 16 carbon atoms and at least one aromatic ring,
- wherein the components (A) and (B) are used at
- 25 weight ratios from 99.9 : 0.1 to 70 : 30, preferably 98 : 2 to 80 : 20.
2. The process of claim 1,
- characterized in that** as metal oxides or metal
- 30 aquoxides, there are employed aluminas, alumina hydrates, especially amorphous alumina hydrates, boehmitic or pseudoboehmitic aluminas, titanium dioxide, aluminum silicate or Si/Al mixed oxides, zirconium oxide, lanthanum oxide, cerium oxide, tin
- 35 oxide, iron oxide, or the mixed oxides thereof.

3. A process according to any one of the preceding claims,  
5 **characterized in that** the organic sulfonic acid is toluenesulfonic acid, preferably *p*-toluenesulfonic acid.
4. A process according to claim 1 or 2,  
10 **characterized in that** the organic sulfonic acid is an organic compound of the R-SO<sub>3</sub>H type, in which R is an alkyl-substituted aromatic hydrocarbon residue with 16 to 24 carbon atoms.
- 15 5. A process according to any one of the preceding claims,  
**characterized in that** the metal oxides or metal aquoxides are brought into contact with the organic sulfonic acid at temperatures from 0 to 380°C, preferably 0 to 90°C.  
20
6. A process according to any one of the preceding claims,  
**characterized in that** the metal oxides or metal  
25 aquoxides are brought into contact with the organic sulfonic acid for a period from 30 seconds to 7 days, preferably 30 to 90 minutes, and preferably with stirring.
- 30 7. A process according to any one of the preceding claims,  
**characterized in that** the modified metal oxides or metal aquoxides are dried by spray drying, freeze drying, microwave drying, drying in supercritical  
35 solvents, filtration or rotary drum drying.

8. A process according to any one of the preceding claims,  
5 **characterized in that** the modified metal oxides/  
metal aquoxides are dispersible in organic solvents  
having a solids content of 10 to 35 wt%, preferably  
10 to 30 wt%.
- 10 9. A process according to any one of the preceding  
claims,  
**characterized in that** the modified metal oxide or  
metal aquoxide is processed into molded articles by  
extrusion, pelleting, or spherical drop forming  
15 processes.
10. A process according to any one of the preceding  
claims,  
**characterized in that** the metal oxides or metal aqu-  
20 oxides are taken up in an organic solvent and this  
solvent is exchanged for another one.
11. Sulfonic acid-modified metal oxides or metal aqu-  
oxides which can be prepared by any one of the pre-  
25 ceding processes.
12. A metal oxide or metal aquoxide dispersion contain-  
ing the sulfonic acid-modified metal oxides/metal  
aquoxides of claim 11 plus at least one organic  
30 viscosity modifier.

13. The metal oxide or metal aquoxide dispersion of  
claim 12,  
5 **characterized in that** the organic viscosity modifier  
is an aqueous dispersion of an organic compound,  
especially a polymeric/oligomeric compound, such as  
cellulose, a cellulose derivative, a polyacrylate,  
or a polyvinyl alcohol.
- 10
14. Use of the sulfonic acid-modified metal oxides or  
metal aquoxides of claim 11,  
**characterized in that** the modified metal oxide/metal  
aquoxide is incorporated as a filler into solvent-  
15 based paints or lacquers or into water-insoluble  
plastics.
15. Use of the sulfonic acid-modified metal oxides or  
metal aquoxides of claim 11 for preparing coatings,  
20 preferably transparent coatings on films/foils,  
metals/metal oxides, glass, PVC and other plastics.
16. Use of the sulfonic acid-modified metal oxides or  
metal aquoxides of claim 11 for the manufacture of  
25 catalyst supports.



**Abstract**

- 5 The present invention relates to a process for preparing metal oxides or metal aquoxides, especially alumina hydrates, which can be dispersed in organic solvents. It also relates to sulfonic acid-modified metal oxides or metal aquoxides which can be prepared by this process.



Fig. 1 / 1

